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EDGEWOOD ARSENAL
TECHNICAL REPORT

EATR 4433

STUDIES IN SOLID-STATE SCIENCE

XI. A TECHNIQUE OF MEASURING THE TRANSPARENCY OF MATERIALS AS A FUNCTION OF TEMPERATURE

by

Thaddeus J. Novak

Edward J. Poziomek

Raymond A. Mackay

September 1970

DEPARTMENT OF THE ARMY
EDGEWOOD ARSENAL
Research Laboratories
Physical Research Laboratory
Edgewood Arsenal, Maryland 21010

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EDGEWOOD ARSENAL TECHNICAL REPORT

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STUDIES IN SOLID-STATE SCIENCE
XI. A TECHNIQUE OF MEASURING THE TRANSPARENCY OF MATERIALS AS A FUNCTION OF TEMPERATURE

by

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September 1970

Task 1T061101A91A15

DEPARTMENT OF THE ARMY
EDGEWOOD ARSENAL
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FOREWORD

The work described in this report was authorized under Task 1T061101A91A15, In-House Laboratory Initiated Research and Development, Molecular Detection and the Mesomorphic State (U). The work was performed between January and June 1970.

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DIGEST

A simple technique has been developed to measure the transparency of materials at any specific wavelength (ultraviolet to near infrared) versus temperature. The procedure involves heating a sample between calcium fluoride plates in a brass holder placed in a Cary-14 spectrophotometer. Changes in transmittance at a fixed wavelength are recorded continuously as the temperature is allowed to change slowly. As an illustration of the procedure, the transmission properties of the nematic liquid crystal butyl *p*-(*p*-ethoxyphenoxycarbonyl)-phenyl carbonate in its various states are described. For comparative purposes a description of the transmittance of phenyl benzoate (which does not possess a mesophase) is also included.

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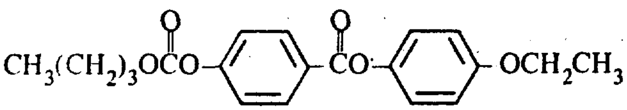
XI. A TECHNIQUE OF MEASURING THE TRANSPARENCY OF MATERIALS AS A FUNCTION OF TEMPERATURE

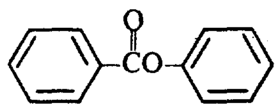
I. INTRODUCTION.

Major interest in the transparency of materials has been with compounds that possess mesophases. In one case, an infrared study was performed with three different mesomorphic cinnamates at various temperatures.* In another case, changes in the transmission of light (from an incandescent lamp) were used to determine phase transition temperatures of various alkali metal stearates.** Chistyakov† studied visible light transparency of several cholesteryl esters as a function of temperature. Using a spectrophotometer, Fergason†† recorded the visible transmission properties of a mixture of cholesteryl esters at several temperatures.

Currently, we are studying effects of bulk impurities on the transparency of mesomorphic materials. We have extended the procedures reported by previous investigators by developing a simple technique of measuring the transparency of various compounds at any particular wavelength versus temperature. As an illustration of the procedure, this paper describes the transmission properties of the nematic liquid crystal, butyl *p*-(*p*-ethoxyphenoxycarbonyl)phenyl carbonate (I), at 4000, 5000, 7000, and 25,000Å. For comparative purposes, a description of the transmittance of phenyl benzoate (II) (which does not possess a mesophase) is also included.



I



II

II. THE CELL ASSEMBLY.

The cell and component parts are shown in figure 1. The construction and assembly are simple. The cell consisted essentially of a heating-tape-wound brass cylinder capable of holding two CaF_2 plates. The heating tape was of the flexible variety (12 mm by 960 cm, 192 watts, 115 volts). The sample was held in a 0.1-mm lead spacer between the salt plates. The spacer was gripped by tightening the brass screw shaft. A surface thermistor probe (4.5 mm diameter, 1.5 mm thick) was mounted in the face of one of the CaF_2 plates. This was accomplished by drilling a hole into the crystal and then setting the thermistor into place with epoxy cement. A groove was also prepared for the thermistor lead. The thermistor sensing surface was set even with the crystal place surface that allowed the sensor to be in contact with the material being studied. It was positioned, however, to avoid obstructing the light path when the cell was placed in the Cary-14 spectrophotometer. An insulated metal ring on a small laboratory jack served as

*Taschek, R., and Williams, D. An Infra-red Study of Several Liquid Crystals. J. Chem. Phys. *6*, 546-552 (1938).

**Benton, D. P., Howe, P. G., and Puddington, I. E. The Mesomorphic Behavior and Anhydrous Soaps. Part 1. Light Transmission by Alkali Metal Stearates. Can. J. Chem. *33*, 1384-1391.

†Chistyakov, I. G. Study of the Transparency of Liquid Crystals. Sov. Phys. Crystallog. *8*, 57-62 (July-August 1963). English transl.

††Fergason, J. L. Cholesteric Structure. I. Optical Properties. Mol. Cryst. *1*, 293-323 (1966).

All dimensions are in millimeters. A Cylindrical brass handle. B Cylindrical threaded brass holder for CaF_2 plates. C Brass screw shaft (dimension refers to shaft diameter less threads). D CaF_2 plates, 25.2 by 5 mm. E Thermistor. F Lead spacer. G Thermistor lead. Heating tape was wound around the handle (A) and the holder (B) but is not shown

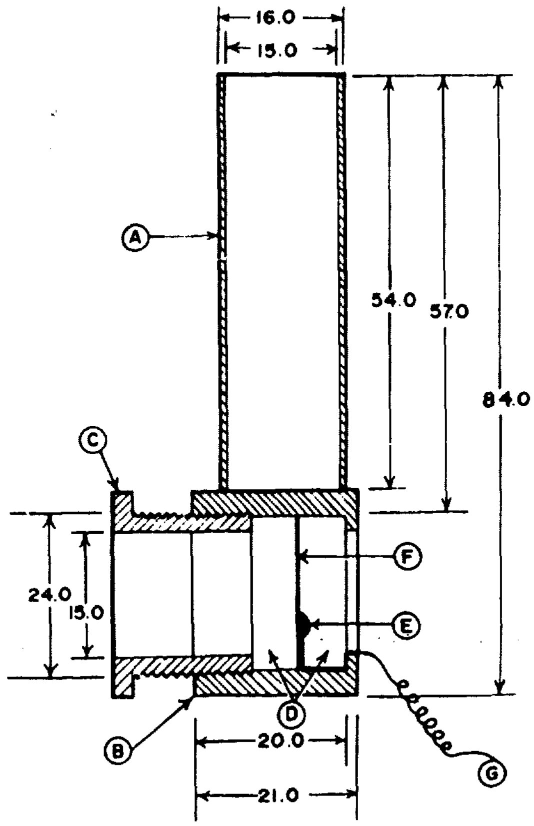


Figure 1. Cell Assembly

the holder for the cell in the spectrophotometer compartment. The position of the holder was preadjusted to provide an unobstructed path for the light beam to pass through the cell at 90° to the plane of the film.

A digital thermistor thermometer (Cole-Parmer) [accuracy ±0.15°C (10° to 90°C), ±0.25°C (90° to 100°C); least significant digit, 0.1°C; reading resolution, 0.02°C] was used as a visual indication of sample temperature.

III. MEASUREMENT OF TRANSMITTANCE.

To obtain a uniform thickness of the sample in the spacer, it was necessary to premelt the material. This was performed by first clamping the cell apparatus with the holder (B, figure 1) in a vertical position. The CaF_2 plate containing the thermistor was placed in the holder with the thermistor facing up. The lead spacer was laid flat on the plate and was oriented so that the thermistor was bottom center of the opening. The compound was placed into the spacer cavity, and the apparatus was heated sufficiently to melt the material. Additional compound was added if needed to fill entirely the spacer opening. When it appeared that a sufficient amount of fused material was present, the second CaF_2 plate was dropped gently onto the spacer. The brass shaft was then screwed into the cylinder. This usually resulted in the crystallization of the sample. The apparatus was heated again until the compound became fluid. The shaft was then tightened

down, causing the sample to assume the 0.1-mm thickness of the spacer. The cell assembly was allowed to cool to room temperature and was placed in the spectrophotometer compartment.

Transmission curves were obtained by allowing the chart to move at 6 mm/min with the wavelength set at the desired value. Other settings on the Cary-14 spectrophotometer included 15 for the slit control and 3 for the dynode switch. The sample heating rate was approximately 0.5°C/min. A nearly linear rate was maintained by supplying current to the heating tape through a variable autotransformer with a motorized attachment that permitted a very slow and continuous change in the transformer setting. Typical results are shown in figures 2 and 3.

Compound I was used as obtained from Princeton Organics, Princeton, New Jersey 08540. Specifications listed it as a high-purity material with a resistivity of 1×10^8 ohm-cm at 85°C. Phenyl benzoate (mp 68° to 69°C) was obtained from Chem Service, Inc., Media, Pennsylvania 19063 and used without purification.

IV. TRANSMISSION EFFECTS.

Figures 2 and 3 illustrate that transitions from solid to mesophase or to isotropic liquid and from mesophase to isotropic liquid are detected easily by marked decrease in light scattering (increase in transparency). Excellent agreement exists for the transition points of the compounds studied irrespective of the wavelength of incident light (table).

Transparency changes from nematic mesophase to isotropic liquid are less dramatic than those that originate from the solid state. The solid-state transitions are preceded by a sharp increase in light scattering and result in the appearance of a peak in the spectral curves. Transparency changes that precede the peak were not reproducible and varied widely at the same and different wavelengths of incident light (figures 4 and 5). The differences undoubtedly reflect changes in crystal texture, molecular reorientation and/or transitions occurring in the solid state.

V. APPLICATIONS.

The technique described in this paper allows a simple means of measuring the transparency of materials to specific wavelengths of light as a function of temperature. It incorporates the sophistication inherent in the capabilities of the Cary-14 spectrophotometer.

One also can use the general procedure to study the absorbance of solutes in several phases of a specific material. In this case, the blank would be the transparency curve of the solvent at the particular temperature chosen for the study.

Table. Transition Temperatures*

Phase changes (compound)	Temp at various incident wavelengths (Å)			
	4000	5000	7000	25000
	°C			
Solid to nematic (I)	57.5-58.0	57.5-57.9	57.5-57.9	57.3-57.7
Nematic to liquid (I)	79.3-79.7	79.3-79.7	79.1-79.6	77.0-78.6**
Solid to liquid (II)	67.7-68.2	67.7-68.1	67.7-68.2	67.5-67.9

*Reported numbers refer to points A-B as illustrated in figures 2 and 3.
**Refers to the beginning and end of a doublet. This was not observed using the other wavelengths of light.

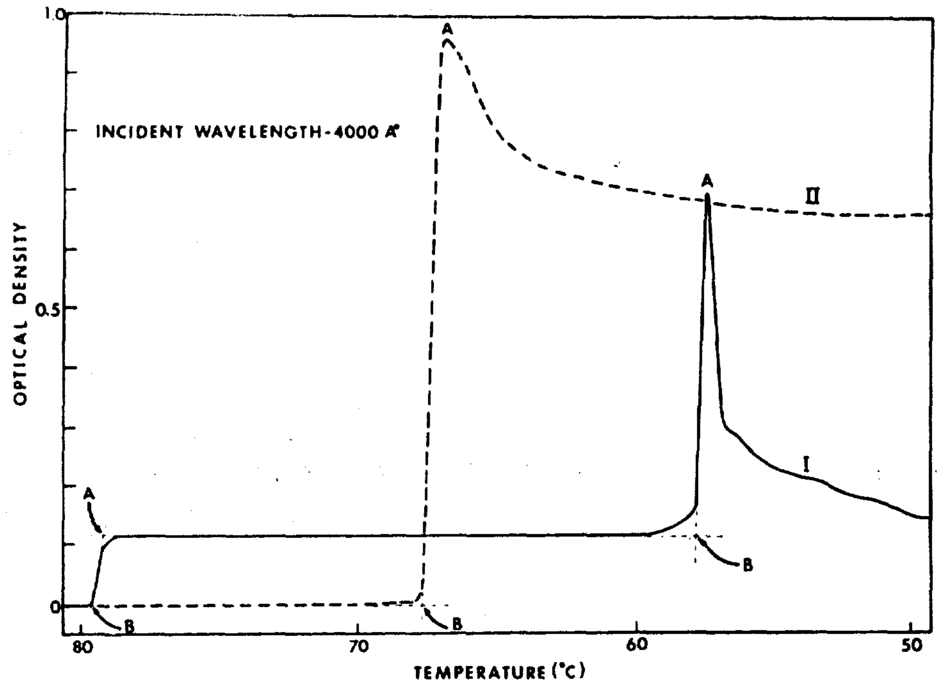


Figure 2. Transparency of Butyl p-(p-ethoxyphenoxycarbonyl)-phenyl Carbonate (_____, I) and Phenyl Benzoate (_ _ _, II) to 4000Å Light.

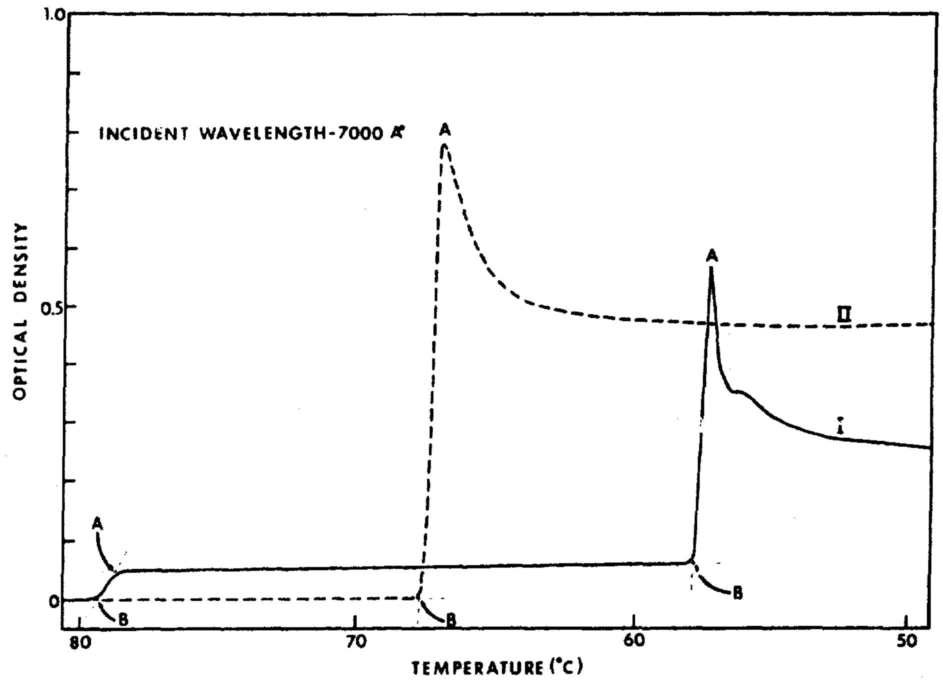


Figure 3. Transparency of Butyl p-(p-ethoxyphenoxycarbonyl)-phenyl Carbonate (_____, I) and Phenyl Benzoate (_ _ _, II) to 7000Å Light.

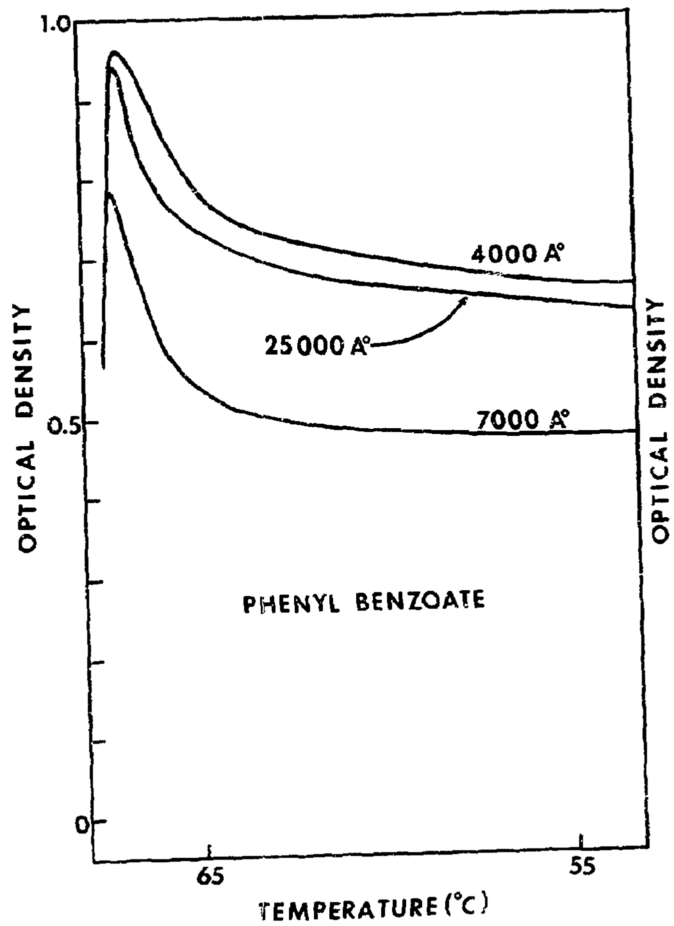


Figure 4. Solid-State Transparency of Phenyl Benzoate to Various Light Wavelengths as a Function of Temperature

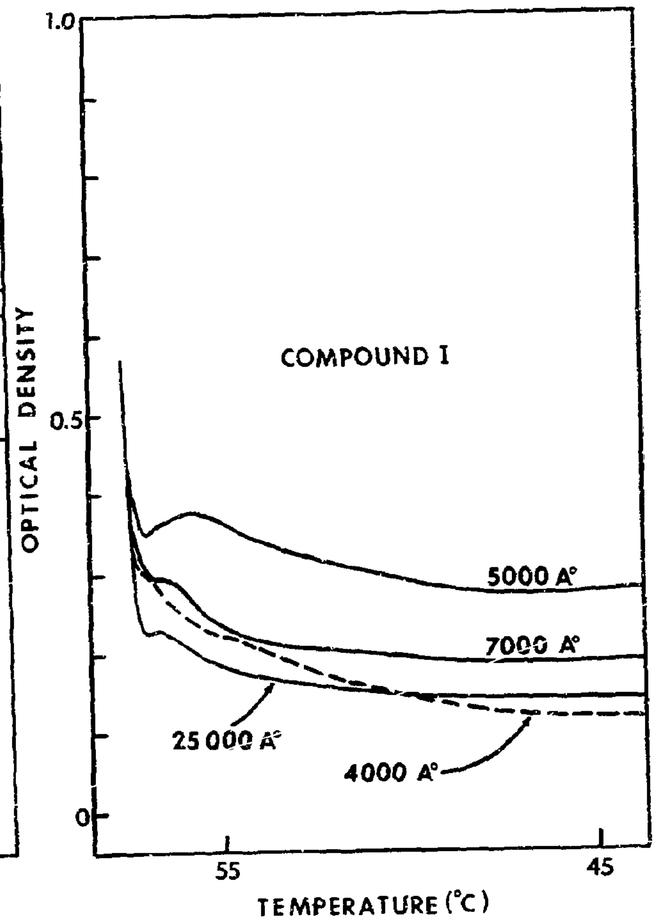


Figure 5. Solid-State Transparency of Butyl *p*-(*p*-ethoxyphenoxycarbonyl)-phenyl Carbonate to Various Light Wavelengths as a Function of Temperature.

Measuring transparency versus temperature also presents a method of characterizing and differentiating solids and mesomorphic materials. Though the present paper describes transparency properties as a function of heating, the corresponding cooling curves can also be obtained easily. This would allow the study of supercooling phenomena.

Another application would be found in the study of the effects of light and heat on the stability of organic materials.

A variety of cell windows can be used depending on the projected use of the technique. Calcium fluoride was our choice because of transparency characteristics and because of superior wetting characteristics with the compounds of interest to us.

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11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
Molecular Detection and the Mesomorphic State	NA

13. ABSTRACT

A simple technique has been developed to measure the transparency of materials at any specific wavelength (ultraviolet to near infrared) versus temperature. The procedure involves heating a sample between calcium fluoride plates in a brass holder placed in a Cary-14 spectrophotometer. Changes in transmittance at a fixed wavelength are recorded continuously as the temperature is allowed to change slowly. As an illustration of the procedure, the transmission properties of the nematic liquid crystal butyl *p*-(*p*-ethoxyphenoxycarbonyl)-phenyl carbonate in its various states are described. For comparative purposes a description of the transmittance of phenyl benzoate (which does not possess a mesophase) is also included.

14. KEYWORDS

Light	Mesophases
Spectroscopy	Defense systems
Liquid crystals	Transparency
Army research	Light scattering
Solids	Nematic

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